"Study of Hetero-molecular Associations in different Polar and Non Polar binary mixtures at Microwave Frequency"

Synopsis

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Research Student

Dnyaneshwar Anandrao Shinde

M.Sc. Physics, PET

Research Guide

Dr. Mahajan Gajanan Ramrao

Head, Assistant Professor
Department of Physics,
Shri Datta Arts, Commerce and Science College,
Hadgaon, Dist.: Nanded
College Code:119
Research Centre: SPS Campus, SRTMU Nanded

1. Introduction

Most of the dielectric relaxation processes reported in the literature were referred for understanding dilute solutions of polar substance in non-polar liquids. Though the non-polar liquid does not itself undergo relaxation but it alters the relaxation time of the solute molecule by reducing the internal field and changing the viscosity. The study of dielectric dispersion and absorption of a binary liquid mixture provides a very sensitive tool for detecting molecular interactions it has been observed that the formation of complexes or the presence of association leads to relaxation times considerably higher than those for the uncomplexed (unassociated) species. The dielectric relaxation studies of polar and non-polar liquids and their mixtures are of great importance to deduce the relation between solute-solvent in the mixture. Study of dielectric behavior of polar and non polar molecules and their mixtures [1-4] under varying conditions of compositions and temperatures has evoked considerable interest.

Dielectric spectroscopy provides an extremely broad frequency range. i.e. from 10^{-4} Hz to 10^{12} Hz therefore it is also known as 'Broadband dielectric spectroscopy'. Dielectric relaxation spectroscopy is sensitive to relaxation process in an extremely wide range of characteristic time i.e. 10^{5} to 10^{-12} (seconds). This spectroscopy has many applications in various fields [5]. The dielectric constant (ε_0) or relative permittivity represents the capacitance of a material relative to that of a vacuum. The capacitance enhancement of a dielectric material arises from the orientation of charges within the material in response to an applied electrostatic field. Charge orientation is often thought in terms of two constituent polarization modes: orientation or rotation polarization in which molecules with permanent dipoles experience an increase in dipole alignment from the thermally driven random orientation, and distortion polarization in which

atomic and electronic polarization occur because of the effect of the applied field on bond lengths, bond angles, and electron distribution within the molecule. Values of dielectric constant therefore characterize the polarizability of the material

Aim of present work is to study dielectric relaxation of polar and non polar liquids using Time Domain Reflectometry Technique.

2. Review of Literature and Development in the subject (previous work done in the relevant area)

In the 18^{th} century Faraday published the first numerical results of measurements on the insulating material, which he called the dielectric. Commercial insulating material, frequently gives complicated results in dielectric measurements because of the presence of a number of different dipole orientation process. Dielectric measurements are sometimes used to obtain information about the structure and interactions between molecules or ions in various materials. 19^{th} and beginning of 20^{th} centuries the dielectric constant was determined for a number of substances, especially for the verification of Maxwell relation. Dielectric materials have in common characters, whether they are solid, liquid or gas, and whether or not they are crystalline in nature, is their ability to store electric energy.

Dielectric materials are electrically non conducting materials. e.g. Glass, ebonite, mica, rubber, wood and paper. All the dielectric materials are insulating materials. But all the insulating materials are not dielectric materials. The difference between a dielectric and an insulator lies in their applications [6-10]. The main function on non-conducting material is to provide electrical insulation, then they are called as insulators and the main function of non-conducting material is store electrical charges, and then they are called as dielectrics.

The literature survey reveals that the dielectric investigations of polar and non polar liquid provide valuable information regarding intermolecular interactions and the consequent structural rearrangement of molecules in solution. The heterogeneous and homogeneous interactions in binary mixtures using dielectric measurements have been studied and reported by several investigators [11-15].

3. Objective of research/Proposed Hypothesis

- To determine complex permittivity of polar and non polar liquids using Time Domain Reflectometry Technique.
- To determine static dielectric constant, dielectric loss and relaxation time at high frequency.
- To determine the Kirkwood correlation factor, Bruggman factor, Thermodynamic Parameters, Excess parameters etc.

4. Methodology to be adapted

Time Domain Reflectometry Technique is the powerful tool to identify the inter- and intra-molecular interactions of the polar liquid and non liquid mixtures. Dielectric studies on mixtures of polar liquids either in the pure state or in the inert solvents have been a subject of interest because they provide useful information regarding molecular complex formation in solution and the structural changes in liquids due to changes in hydrogen bonding. The relative changes in dielectric parameters are important to predict structural changes in liquid.

Time Domain Technique (TDT) gives dielectric relaxation study over a wide high frequency range. The basic Time domain technique consists of fast rising pulse generator,

sampling unit and a wide band sampling oscilloscope. A voltage pulse propagated in the coaxial line until it reaches the air dielectric interface, where a part of pulse is reflected and the rest is transmitted through the dielectric sample. It is possible to determine the dielectric properties of the substances by analyzing reflection coefficient. A Time domain dielectric relaxation spectroscopy determines the response of sample to an applied electric field in terms of the complex permittivity.

Time Domain Technique has been used to get complex permittivity spectra of various materials like solids [16], organic liquids [17-20], aqueous solutions [21, 22], electrolytic solutions [23-26], biological materials [27], agricultural samples [28] and biological samples [29-33]. Also studies of dielectric behavior of polar mixtures at different concentration and temperatures have led to valuable information regarding hydrogen bonding and solute-solvent interaction [34-37].

5. Importance of study/ Society Application:

As polar and non polar liquids have wide applications of in nearly every field of science, engineering & technology. It is indeed important to look into its molecular interaction, structural and dynamical properties using spectroscopic methods.

International/ National Status:

The following scientists are actively doing research in this field at international/National level:

- S Yaghara, University of Tokyo, Japan
- S Sudo, dept. of Physics, Tokyo city University, Tamazustumi, Setagaya, Tokyo
- N Shiyanshiki, University of Tokyo, Japan.

- Udo Kaatze, DrittesPhysikalischesInstitut Georg-August-Universitat Gottingen, Germany.
- S.C. Mehrotra, Dr. BAMU, Aurangabad(MS).
- A C Kumbharkhane, SRTM University, Nanded, Maharashtra
- R.J. Sengwa, Jodhpur, JNV University, Jodhpur(RS).
- V A Rana, Gujrat University, Ahmedabad, Gujrat

Significance of the study

The dielectric and structural relaxation measurements of polar and non polar solution using a TDR make a gigantic impact on the elementary study. Therefore, this study will be helpful in understanding the structural and dynamical behavior of molecules in different environment (i.e. temperature, concentration, etc.) using the dielectric parameters like dielectric permittivity, dielectic constant, relaxation time etc.

6. Proposed work Plan/ Formulation and Structure of Study

- ✓ **First Year:** Literature survey, solvents selection for experimental work.
- ✓ **Second Year**: Dielectric measurement of polar and non polar solutions. Extract the dielectric parameters such as static dielectric constant, relaxation time, dielectric constant at high frequency and Kirkwood correlation factor.
- ✓ **Third year**: Study the dielectric and structural behavior through the dielectric relaxation parameters. These interpretations will be published by writing research papers or presenting the work in conference/seminars. Finally, write up thesis and complete the research work.

7. References

[1] G. Moumuzias, D.K. Panopoulos, G. Ritzoulis, J. Chme. Eng. Data 36 (1991) 20.

[2] G.E. Papanastasiou, I. I. Zlogas; J. Chem. Eng. Data 37 (1992) 167.

[3] R. Payne, I.E. Theodorou; J. Chem. Eng. 76 (1972) 2892.

[4] M. Tabellout, P. Lanceleur, J. R. Emergy, D. Hayward, R. Peltrick; J. Chem. Soc. Faraday Trans. 86 (1990) 1493.

[5] F Kremer, A Schönhals. 'Broadband Dielectric Spectroscopy', Springer 2003.

[6] C. P. Smyth, Dielectric behavior and structure, McGraw-Hill Book Co., New York (1955).

[7] B. Tareev, Physics of Dielectric Material, Mir Publishers, Moscow (1975).

[8] C. J. F. Bottcher, Theory of Electric Polarization, Elsevier, Amsterdam (1952).

[9] N. E. Hill, W. E. Vaughan, A. H. Price and Davies, Van Neatrand Reinhold co., London (1970).

[10] J. B. Hasted, "Aqueous dielectric" Chapman and Hall Ltd., London (1973).

[11] A. Mohan, M. Malathi, S. S. Shaikh, A. C. Kumbharkhane, J Solution Chem (2016) 45:221–234.

[12] Kumar, P.M., Malathi M ; J. Mol. Liq. 145, 5–7 (2009)

[13] Joshi, Y.S., Kumbharkhane, A.C.; Fluid Phase Equilib. 317, 96–101 (2012).

[14] Sengwa, R.J., Madhvi, S.S., Sharma, S.; J. Solution Chem. 35, 1037–1055 (2006).

[15] Wohlfarth, C.; Landolt-Bornstein:Numerical Data and Functional Relationships in Science and Technology—Physical Chemistry, vol. 17.Springer, Heidelberg (2008).

[16] K. Baba, T. Yamaki, T. Fujimura, *Japanese J. of Appl. Phys*. 24, 1532 (1985).

[17] R. H. Cole, J. G. Berberian, S. Mashimo, G. Chryssikos, A. Burns, E. Tombari, *J. Appl. Phys.* 66, 793 (1989).

[18] D. Bertolini, M. Cassettari, G. Salvetti, M. Tomabari ans S. Veronesi, *Rev. Sci. Instru.* 61, 450 (1990).

[19] S. C. Mehrotra, B. Gestblom and J. Sjoblom, *Finn. Chem. Lett.* 34, (1985).

[20] A. Suggett, P.A. Mackness, M. J. Tait, *Nature.* 228, 456 (1970).

[21] B. Gestblom, H. Elmgren, *Chemical Physics Letters*. 90, 412 (1982).

[22] B. Gestblom, J. Sjoblom, *J. Phys. Chem.* 90, 4175 (1986).

[23] B. Gestblom, S.C. Mehrotra, J. Sjoblom, *J. of Solu. Chem.* 15, 55 (1986).

[24] B. Gestblom, J. Songstand, *Acta. Chemica Scandinavica.* B14, 396 (1987).

[25] W. Paul, R. H. Cole, *J. Phys. Chem.* 86, 2486 (1982).

[26] B. Gestblom, I. Svorstol, J. Songstand, *J. Phys. Chem.* 90, 4684 (1986).

[27] C. Gebriel, E. H. Grant, R. Tata, P. R. Brown, B. Gestblom, E. Norland, *Nature.* 328, 145 (1987).

[28] B. P. Kwark, S.O. Nelson and E. Bahar, *IEEE-Trans. Instrum. Measu.* IM-28, 109 (1979).

[29] M. Kent, *J. Microwave power.* 10, 37 (1975).

[30] M. S. Iskander and S. S. Stuchly, *IEEE-Trans. Instrum. Measu.* IM-21, 425 (1972).

[31] N. R. V. Nightingle, A. W. J. Dawkins, R. J. Sheppard, E. H. Grant, V. D. Goodridge and J. L. Christe, *Phys. Med. Miol.* 25, 1161 (1980).

[32] Komal B. Kabara , Kunal H. Wananje, Ashok C. Kumbharkhane , Arvind V. Sarode ; Journal of Molecular Liquids, Vol.1 February 2020, 112137.

[33] Dalia El Khaled, Nuria N. Castellano, Jose A. Gázquez, Alberto-Jesus Perea-Moreno, and Francisco Manzano-Agugliaro; Materials (Basel). 2016 May; 9(5): 310.

[34] D. Gopalakrishnan,V. Balachandar, A.C. Kumbharkhane, R. Sampathkumar, International J. Biological Macromolecules. 138 (2019) 215-223.

[35] A C Kumbharkhane, YS Joshi, SC Mehrotra et.al. Physica B, 421 1 (2013)

[36] P. SenthilKumar, K.Vinoth, T.Ganesh, M.Maria Sylvester, A. Karunakaran, A.R. Deshmukh, P. Hudge, T. Ganesh, A.C. Kumbharkhane, Current Appl. Phys. 38 (2022) 7-14.

[37] A.G. Gubre, A.C. Kumbharkhane, Journal of the Indian Chemical Society, Vol.100, Issue 6, June 2023, pages 101016.

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